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A classical approach to dissociative electron attachment DA: application to temperature effects in the DA cross section of CF_3Cl

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Abstract

A classical theory of dissociative attachment (DA) is developed. The DA cross section $\sigma_{v\to DA}$ of a molecule in the initial vibrational state v is calculated. The model is applied to the negative ion formation in low energy electron scattering from CF_3Cl molecules. Temperature effects of the DA cross section of CF_3Cl can be explained within our classical model.

1. Introduction

Quantum mechanics clearly provides the proper description of dissociative attachment (DA) [1–3], but it is nevertheless of interest how well simpler models are able to describe the process. In this Letter, we present a simple instructive classical model of DA and show for the example CF_3Cl that it is possible to understand DA within this model.

Scattering of low energy electrons from chlorofluoromethanes has been the subject of various experimental investigations within recent years [4–9]. Measurements of the DA of these molecules have also been carried out [10–14]. Recently interesting temperature effects in the DA of CF_3Cl for impact energies less than ≈ 3 eV were reported [13] (see also Fig. 4a below). A primitive quantum dynamical approach [13] could explain some but not all of the features. In this work we show that it is possible to account for the experimental data within a simple classical model. A short summary of the experimental results for low energy electron scattering by CF_3Cl is given in Section 2 together with a description of the model. For details see Refs. [4,7,10–13,15]. In Section 3 a classical theory of DA is developed, in close analogy to the classical theory of Penning ionization given by Miller [16]. Results of its application to CF_3Cl are shown and discussed in Section 4. Section 5 contains some concluding remarks and an outlook for future projects.

2. Experimental findings and model

For impact energies less than 3 eV resonant scattering from CF_3Cl is due to electron attachment to the $a_1(C\text{–}Cl\ \sigma^*)$ orbital [4,17–19] which is the LUMO of CF_3Cl. The total cross section of CF_3Cl shows a resonance at 2.0 eV [4,15]. Quantum chemically calculated vertical electron affinities of CF_3Cl

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are in accord with the position of this resonance [4,17–19]. The elastic and inelastic cross sections show corresponding peaks at approximately 2 eV. Resonant inelastic scattering is by far dominated by (single) vibrational excitation VE of the C–Cl strechning mode ν_3 [7],

$$CF_3\text{–}Cl(v_{\nu_3}=0)+e \rightarrow CF_3\text{–}Cl(v_{\nu_3}=1)+e.$$

In measurements of the dissociative attachment DA only Cl^- ions can be detected in this energy range,

$$CF_3\text{–}Cl+e \rightarrow CF_3+Cl^-.$$

The respective peak appears at significantly lower energy ($\approx$ 1.4 eV) [10,12–14,20] than the peaks in the elastic and inelastic cross sections (2 eV). The excess energy of the fragments is mainly released as translational energy [11], i.e. on the time scale of the dissociation ($\approx$ 10 fs, see Ref. [13]) there is no significant internal vibrational energy redistribution IVR.

The Cl^- ion yield of CF_3Cl is remarkably lower than that of the other chlorofluoromethanes [10,11] and CCl_4. Besides CF_3Cl is the only of these molecules which shows high translational energy of the fragments for the respective resonance. This indicates that the lowest resonance of CF_3Cl is very short-lived and unstable with respect to autodetachment. Thus the DA cross section is much smaller than the (resonant + direct) elastic and inelastic scattering cross sections. Measurement of absolute DA cross sections of this molecule give values of 1.7×10^{-2} Å^2 (300 K) [12] and 3.9×10^{-2} Å^2 (400 K) [14] for the peak maximum of the lowest resonance. The latter is probably more reliable since the width of the peak in the swarm-experiment [12] is only two thirds of the one found in all beam-experiments. Correcting the value from Ref. [14] for the temperature effect [12,13] (see also below) the absolute DA cross section amounts to 3.7×10^{-2} Å^2 at 300 K. With the results of Ref. [7] this yields a ratio of the DA cross section to the elastic and inelastic cross sections of $\approx$ 1:600 and 1:300 at their respective maxima. Yet there may be some uncertainty of the value obtained from Ref. [14], since the ratio of the current resonance to the next higher one differs considerably (up to one order of magnitude) in all measurements [10,12,14,20].

Thus experimental data and calculations show that

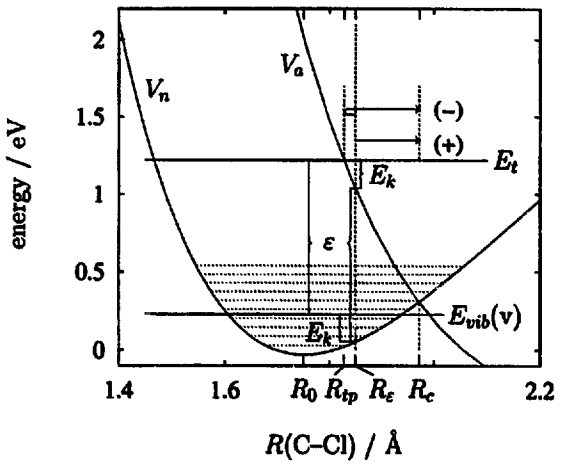

Fig. 1. The transition from V_n via the anion state V_a to dissociation is illustrated for a specific value R_ε of the C–Cl-distance and the vibrational energy $E_{vib}(v=4)$ (see text). The dotted lines indicate the energy intervals $[E_{vib}(v-\frac{1}{2}), E_{vib}(v+\frac{1}{2})]$ for the vibrational levels $v=0,\ldots,9$ used in this calculation. The energy level $v=4$ is fully allowed in this example, whereas $v=1$ is only partly allowed and $v=0$ is forbidden (see text).

for impact energies less than $\approx$ 3 eV electron scattering from CF_3Cl affects primarily the C–Cl bond. To a good approximation one can therefore restrict the description of the behavior of this resonance to one degree of freedom – the C–Cl bond – and neglect other vibrational modes. For the application of our classical theory we use the model potentials already published in Ref. [13], the relevant parts of which are shown in Fig. 1. Both are Morse potentials. The Franck–Condon distance was chosen according to the position of the resonance in the total scattering cross section and to the calculated vertical electron affinities (2 eV). The steepness of the anion potential in this region was estimated by mirroring the density of the neutral molecule to the total scattering cross section σ_{tot} in Ref. [15]. This procedure ensures that the relevant part of the initial density which undergoes DA is reflected onto the DA part of σ_{tot}. In addition, the dissociation time τ_d which a wavepacket needs to move from the Franck–Condon region to the crossing point of the potentials, R_c, is 10 fs, which is an upper limit for the resonance lifetime estimated from the experiments. The Heisenberg principle is well fulfilled (in atomic units: $\tau_d \Delta E \approx 14 > \hbar = 1$, where ΔE is the half-width of the signal in σ_{DA}). In order to yield a

better estimate, quantum calculations of the potential surface are desirable. For further details about the model potentials, see Ref. [13].

The DA cross section of CF_3Cl shows strong temperature effects [13]: A new threshold peak close to 0 eV appears as the temperature rises. At 300 K it is hardly visible, but at 800 K this peak is the dominant feature. The peak at 1.4 eV (300 K) is shifted to 1.1 eV (800 K) and its intensity is doubled whereas a peak at 4.8 eV in the ion-yield-curve of Cl^- remains basicly unchanged [13]. In the energy range of 3–6 eV several products of DA occur [10]. This corresponds to broad structures in the total and inelastic cross sections around 5.8 [15] and 5.5 eV [7], respectively. Different assignments of these structures can be found in the literature [4,7].

3. Classical Theory of DA

The classical approach given below describes the dissociative attachment DA of quasi-two-atom molecules,

$$AB + e \rightarrow A + B^-, \tag{1}$$

where A and B may be atoms or groups of atoms whose internal degrees of freedom can be neglected, such that only one dissociative exit channel exists for a given resonant state and the dissociation can well be described in a one-dimensional model.

The derivation is formulated in close analogy to a classical theory of Penning ionization PI and associative ionization AI,

$$A^* + B \rightarrow A + B^+ + e \quad (PI),$$
$$A^* + B \rightarrow AB^+ + e \quad (AI), \tag{2}$$

given by Miller [16]. If there is one electron more involved, the overall problem remains very similar. The respective processes are called collisional detachment CD and associative detachment AD,

$$A^- + B \rightarrow A + B + e \quad (CD),$$
$$A^- + B \rightarrow AB + e \quad (AD), \tag{3}$$

the latter of which is the reverse process of DA (1).

The cross section for dissociative attachment of electrons with kinetic energy ϵ to a molecule in the initial vibrational state v is given by

$$\sigma_{v \rightarrow DA}(\epsilon) \approx \frac{\pi}{k^2}(2l+1)P_{v \rightarrow DA}(\epsilon). \tag{4}$$

The approximation (4) implies that only a single partial wave l contributes to the DA process which is often the case [21].

Now we wish to find an expression for the probability $P_{v \rightarrow DA}(\epsilon)$. Consider for example the transition outlined in Fig. 1. The neutral molecule (potential curve V_n) vibrates with energy E_{vib}. At the internuclear distance R_ϵ an electron is attached, i.e. the system goes from a continuum state (AB + e) to the discrete state (AB^-). The rate of this transition is – for reasons of micro-reversibility – the same as of the reverse autodetachment, $\Gamma(R_\epsilon)/\hbar$, where $\Gamma(R_\epsilon)$ is the (local) width of the resonance.

We assume a Franck–Condon-like transition to the anion state V_a. This implies two important points: Firstly, the transition is vertical such that R_ϵ remains constant. From this it follows that the kinetic energy ϵ of the electron is related to R_ϵ via

$$\epsilon(R_\epsilon) = V_a(R_\epsilon) - V_n(R_\epsilon). \tag{5}$$

Secondly, the (relative) momentum of the nuclei is conserved and so is their kinetic energy E_k. Neglecting the rotational energy of the molecule, the total energy E_t after the transition can therefore be calculated according to

$$\begin{aligned} E_t &= E_{vib} + \epsilon(R_\epsilon) \\ &= V_a(R_\epsilon) + E_k(R_\epsilon) \\ &= V_a(R_\epsilon) + [E_{vib} - V_n(R_\epsilon)]. \end{aligned} \tag{6}$$

After the transition the nuclei may with equal probability separate directly (+) or first approach the classical turning point R_{tp} (where $E_t = V_a$) and afterwards move towards dissociation (−). Accordingly $P_{v \rightarrow DA}(\epsilon)$ consists of two terms,

$$P_{v \rightarrow DA}(\epsilon) = P^{(+)}_{v \rightarrow DA}(\epsilon) + P^{(-)}_{v \rightarrow DA}(\epsilon). \tag{7}$$

In order to contribute to the DA cross section, the anion state created at R_ϵ must survive on either way until the nuclei have separated so far that either the molecule can be considered dissociated or the coupling of the discrete state to the continuum has disappeared, i.e. $\Gamma(R) \approx 0$, such that the system can no longer escape into the continuum. If the potential curves cross at some point R_c, as in Fig. 1, it is sufficient that the anion reaches this point, since for $R > R_c$ it is more stable than the neutral species and leakage into the continuum ($V_n + \epsilon$) is impossible.

Thus the anion *must* dissociate once the internuclear distance has reached R_c.

With the above considerations we may write the probability $p_{DA}^{(\pm)}(R_\epsilon)\,dR_\epsilon$ for the dissociative attachment of a molecule with internuclear distance between R_ϵ and $R_\epsilon + dR_\epsilon$,

$$p_{DA}^{(\pm)}(R_\epsilon)\,dR_\epsilon = \frac{\gamma(R_\epsilon)}{\hbar}\frac{dR_\epsilon}{|v(R_\epsilon)|}P_S^{(\pm)}(R_\epsilon, R_c), \tag{8}$$

where $dR_\epsilon/|v(R_\epsilon)| = dt$ is the time the molecule spends between R_ϵ and $R_\epsilon + dR_\epsilon$. The absolute value of the velocity of the nuclei $|v(R_\epsilon)|$ is given by

$$|v(R_\epsilon)| = \sqrt{\frac{2}{\mu}[E_{vib} - V_n(R_\epsilon)]}$$

$$= \sqrt{\frac{2}{\mu}[E_t - V_a(R_\epsilon)]}\,. \tag{9}$$

The probability $P_S(R_1, R_2)$ for a molecule to survive in the discrete (anion) state between R_1 and R_2 obeys the integral equation

$$P_S(R_1, R_2) = 1 - \int_{R_1}^{R_2}\frac{\Gamma(R)}{\hbar|v(R)|}P_S(R_1, R)\,dR. \tag{10}$$

The second term on the right-hand side is the probability that the system escapes into the continuum somewhere in the range under consideration. The solution of Eq. (10) is

$$P_S(R_1, R_2) = \exp\left(-\int_{R_1}^{R_2}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right). \tag{11}$$

This expression for the survival probability was also derived by O'Malley [1] in a quantum mechanical approach.

Using (11) we obtain for the (+) and (−) paths in (8),

$$p_{DA}^{(+)}(R_\epsilon)\,dR_\epsilon = \frac{\Gamma(R_\epsilon)}{\hbar|v(R_\epsilon)|}\exp\left(-\int_{R_\epsilon}^{R_c}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right)dR_\epsilon,$$

$$p_{DA}^{(-)}(R_\epsilon)\,dR_\epsilon = \frac{\Gamma(R_\epsilon)}{\hbar|v(R_\epsilon)|}\exp\left(-2\int_{R_{tp}}^{R_\epsilon}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right) \times \exp\left(-\int_{R_\epsilon}^{R_c}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right)dR_\epsilon \tag{12}$$

which with the help of (7) leads to

$$p_{DA}(R_\epsilon)\,dR_\epsilon = \frac{\Gamma(R_\epsilon)}{\hbar|v(R_\epsilon)|}\exp\left(-\int_{R_\epsilon}^{R_c}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right) \times\left[1 + \exp\left(-2\int_{R_{tp}}^{R_\epsilon}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right)\right]dR_\epsilon. \tag{13}$$

In order to find the DA probability for a vibrational state v we perform a coordinate transformation. If the function $\epsilon(R_\epsilon)$ in Eq. (5) is monotonic, as in the case of Fig. 2b, then

$$\tilde{p}_{DA}(\epsilon)\,|d\epsilon| = p_{DA}(R_\epsilon)\,|dR_\epsilon|$$

$$\Leftrightarrow \tilde{p}_{DA}(\epsilon) = p_{DA}(R_\epsilon)\frac{1}{|d\epsilon/dR_\epsilon|}$$

$$= p_{DA}(R_\epsilon)\frac{1}{|\epsilon'|}. \tag{14}$$

If in Eq. (6) we keep the total energy E_t constant, we have

$$d\epsilon = -dE_{vib}. \tag{15}$$

Thus we may rewrite Eq. (13),

$$\tilde{p}_{DA}(E_{vib})\,dE_{vib} = \frac{\Gamma(R_\epsilon)}{\hbar|v(R_\epsilon)||\epsilon'|}\exp\left(-\int_{R_\epsilon}^{R_c}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right) \times\left[1 + \exp\left(-2\int_{R_{tp}}^{R_\epsilon}\frac{\Gamma(R)}{\hbar|v(R)|}\,dR\right)\right]dE_{vib}. \tag{16}$$

Finally we introduce a quantization via integration over intervals of the vibrational energy E_{vib} and obtain for $P_{v\to DA}$

$$p_{v\to DA}([\epsilon, \epsilon + \Delta\epsilon]) \equiv P_{v\to DA}(\bar{\epsilon}) = \int_{E_{vib}(v-1/2)}^{E_{vib}(v+1/2)}\tilde{p}_{DA}(E_{vib})\,dE_{vib}. \tag{17}$$

Because of Eq. (15), the right-hand side of Eq. (17) corresponds to an interval $[\epsilon, \epsilon + \Delta\epsilon]$. We assign it to the average value $\bar{\epsilon}$ of this interval.

The integral in Eq. (17) can be approximated according to

$$P_{v\to DA}(\bar{\epsilon}) = \tilde{p}_{DA}(E_{vib}(v)) \times \left[E_{vib}\left(v+\tfrac{1}{2}\right) - E_{vib}\left(v-\tfrac{1}{2}\right)\right]. \quad (18)$$

The interval $[E_{vib}(v-\frac{1}{2}), E_{vib}(v+\frac{1}{2})]$ is not for all values of $V_n(R_{\bar{\epsilon}})$ classically allowed. Three cases can be distinguished (see also Fig. 1),

– $V_n(R_{\bar{\epsilon}}) > E_{vib}(v+\frac{1}{2})$. The vibrational level v is not allowed, such that

$$P_{v\to DA}(\bar{\epsilon}) = 0. \quad (19)$$

– $E_{vib}(v-\frac{1}{2}) < V_n(R_{\bar{\epsilon}}) < E_{vib}(v+\frac{1}{2})$. The interval $[V_n(R_{\bar{\epsilon}}), E_{vib}(v+\frac{1}{2})]$ is allowed. Eq. (18) is replaced by

$$P_{v\to DA}(\bar{\epsilon}) = \tilde{p}_{DA}\left(\bar{E}_{vib}\right)\left[E_{vib}\left(v+\tfrac{1}{2}\right) - V_n(R_{\bar{\epsilon}})\right], \quad (20)$$

where $\bar{E}_{vib} = \frac{1}{2}[E_{vib}(v+\frac{1}{2}) + V_n(R_{\bar{\epsilon}})]$.

– $V_n(R_{\bar{\epsilon}}) < E_{vib}(v-\frac{1}{2})$. The full interval is allowed.

The dissociative cross section at a given temperature can be calculated from the vibrational cross sections $\sigma_{v\to DA}$ using the Boltzmann-distribution,

$$\sigma_{DA}(T) = \sum_v \frac{\exp(-E_{vib}(v)/kT)}{Q}\sigma_{v\to DA}(\bar{\epsilon}) = \frac{\pi\hbar^2(2l+1)}{2m_e\bar{\epsilon}Q}\sum_v \exp\left(\frac{-E_{vib}(v)}{kT}\right) \times P_{v\to DA}(\bar{\epsilon}), \quad (21)$$

with

$$Q = \sum_v \exp\left(\frac{-E_{vib}(v)}{kT}\right).$$

To include the effects of rotation of the molecule one simply adds the centrifugal potential, $J(J+1)\times\hbar^2/2\mu R^2$, to the anion and neutral potentials. Since J is typically $\gg 1$, and the electron carries only ≈ 0, 1, or 2 units of angular momentum, it is usually a good approximation to neglect the change of J caused by the electron. Therefore the $V_a - V_n$ is independent of J, such that the position of R_c remains unchanged. In addition there is a J-dependence in the classical velocity (see Eqs. (9) and (13)) which enters, in principle at least, the Boltzmann averaging. For J not exceedingly large, however, this rotational effect should be small and neglible.

4. Application to temperature-dependent dissociative attachment of CF_3Cl: results and discussion

From symmetry considerations [21] and from the isotropic angular distribution of the vibrational excitation of the ν_3-mode [7] it must be concluded that the resonant scattering from the a_1-orbital arises almost exclusively from the partial wave $l = 0$.

We use two trial functions Γ_1 and Γ_2 for the resonance width Γ which are depicted in Fig. 2a. Γ_1 is determined within the following model: Semiclassically, Γ is a function of R_ϵ. If ϵ grows monotonically as R_ϵ decreases (which is the case here) such that there is no second crossing point for small R_ϵ, then $\Gamma(R_\epsilon)$ should be an exponential function [22,23]. According to this we set: $\Gamma(R_\epsilon) = a\exp[-(R_\epsilon - R_0)/b]$, where $a = 0.93$ eV and $b = 0.073$ Å. This is represented by the solid curve in Fig. 2a. But for $R_\epsilon \geq R_c$, $\Gamma(R_\epsilon)$ must be exactly zero. This behaviour cannot be described in terms of an exponential function. Here we adopt results from the quantum mechanical description of threshold phenomena. Since R_ϵ and ϵ are connected (Eq. (5)), Γ can also be expressed as a function of ϵ. According to Wigner $\Gamma(\epsilon) \sim \epsilon((2l+1)/2)$ for $\epsilon \to 0$ [3,24]. Since we have $l = 0$ in this case, we get $\Gamma(\epsilon) = c\sqrt{\epsilon}$, where we put $c = 0.20\sqrt{\text{eV}}$. This part is represented by the dotted curve. Γ_2 is modified in the threshold-part according to the dashed line in Fig. 2a such that Eq. (21) would reproduce the experimental data at $T = 300$ and 800 K. The results for Γ_1 and Γ_2 differ only quantitatively, as can be seen in Fig. 4b.

Fig. 2b shows the best fit function Γ_2 for the resonance width plotted as a function of the kinetic energy ϵ. In Fig. 2d dissociative cross sections $\sigma_{v\to DA}$ are depicted which are calculated with Γ_2. For reasons of clearness of the plot the $\sigma_{v\to DA}$ are

given only for the vibrational levels $v = 0, 1, 2, 3$. Going from Fig. 2d along the solid straight lines to Fig. 2c it can be seen that:

(i) For a vibrational level v the cross section $\sigma_{v\to DA}$ starts at an appearance energy $\bar{\epsilon}_a$ such that $V_n(R_{\bar{\epsilon}_a}) = E_{vib}(v + \frac{1}{2})$ (Fig. 2c). The level $v = 5$ has an appearance energy of 0 eV. Levels with $v > 5$ are allowed for all (relevant) $R_{\bar{\epsilon}}$ and appear also at 0 eV.

(ii) The smaller v the greater is the appearance energy $\bar{\epsilon}_a$. Therefore the lowest possible resonance width Γ and distance from the crossing point R_c right after the transition to the anion state increase as well. This results in a small survival probability and ultimately in a small maximum value of the cross section $\sigma_{v\to DA}$. The maxima of the $\sigma_{v\to DA}$ rise fast with increasing values of v, since the location of the crossing point at an energy, which is low compared to the ranges of the vibrational levels, causes large relative differences between the minimum distances from the crossing point $(R_c - R_{\bar{\epsilon}_a})$ for different levels (if $v \leqslant 5$) and thus large differences in the survival probabilities $P_S(R_{\bar{\epsilon}_a}, R_c)$.

(iii) The cross section $\sigma_{v\to DA}$ shows a break for $V_n(R_{\bar{\epsilon}}) = E_{vib}(v - \frac{1}{2})$.

(iv) $\sigma_{v\to DA}$ has its maximum at a value $\bar{\epsilon}$ such that $E_{vib}(v - \frac{1}{2}) < V_n(R_{\bar{\epsilon}}) < E_{vib}(v + \frac{1}{2})$. This can be explained as follows: the survival probability $P_S(R_{\bar{\epsilon}}, R_c)$ increases monotonically as $R_{\bar{\epsilon}}$ approaches R_c, but for $R_{\bar{\epsilon}}$ with $E_{vib}(v - \frac{1}{2}) < V_n(R_{\bar{\epsilon}})$ the classically allowed interval decreases.

(v) If in an energy interval $[\bar{\epsilon}_1, \bar{\epsilon}_2]$ several vibrational levels are fully allowed, then the cross section of the highest level is the smallest (for example, in the range [0.8 eV, 1.1 eV], $\sigma_{3\to DA} < \sigma_{2\to DA}$). This is because the velocity of the nuclei rises as v, such that the neutral molecule in the higher vibrational state has less time for the transition to the anion state (compare for example, Eq. (8)).

In addition it can be said that the cross section $\sigma_{v\to DA}$ of a vibrational level v is indeed mainly influenced by the corresponding range of the width Γ indicated in Fig. 2.

Fig. 3 shows, as was explained in (ii), the strong increase of the maximum values of the $\sigma_{v\to DA}$ up to

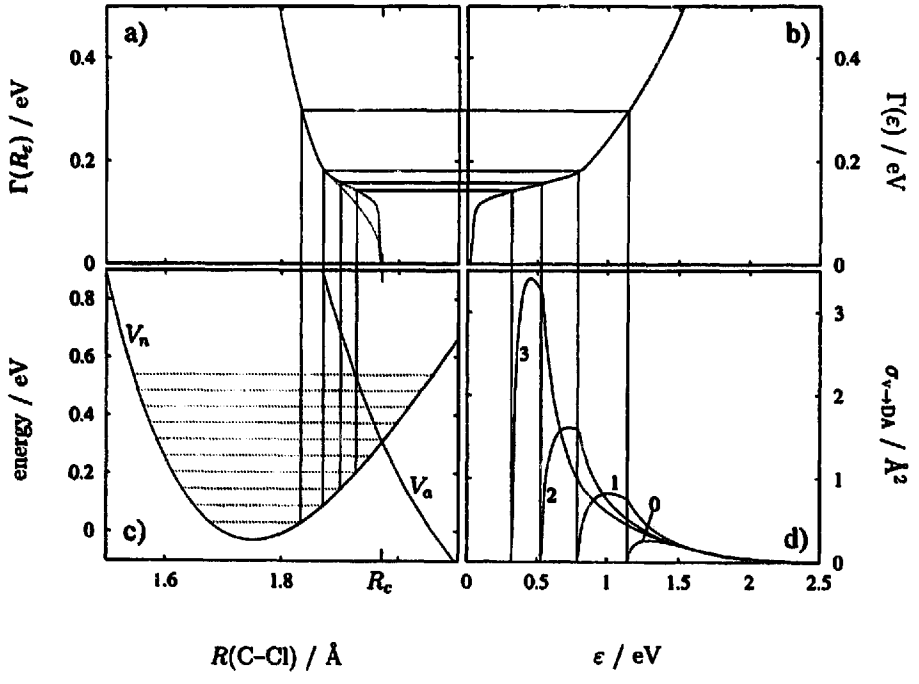

Fig. 2. (a) The trial functions Γ_1 and Γ_2 for the resonance width used in this calculation, plotted as a function of the internuclear distance R_ϵ. (b) Γ_2, plotted as a function of the kinetic energy of the electron. (c) Potential curves as in Fig. 1. (d) Dissociative cross sections $\sigma_{v\to DA}$ for $v = 0, 1, 2, 3$. The solid straight lines indicate the correspondence of the dominant parts of the $\sigma_{v\to DA}$ to certain parts of the resonance width and to the respective ranges of the kinetic energy $\bar{\epsilon}$ where $E_{vib}(v - \frac{1}{2}) < V_n(R_\epsilon) < E_{vib}(v + \frac{1}{2})$ (see text).

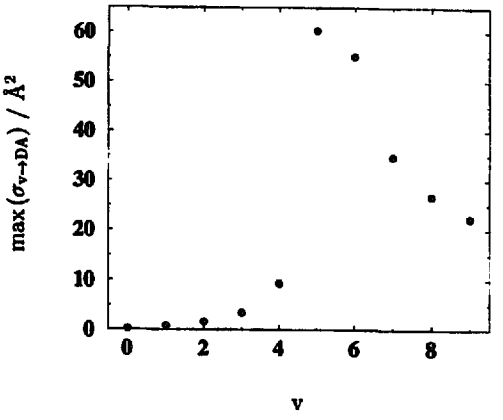

Fig. 3. The maxima of the cross sections $\sigma_{v\to DA}$ plotted as a function of the vibrational quantum numbers v, calculated with Γ_2.

$v = 5, 6$, which is the energetic range of the crossing point, and a considerable decrease for $v > 6$ because of (i) and (v). The consequence of the location of the crossing point R_c for the $\sigma_{v\to DA}$ was confirmed experimentally by Külz et al. for Na_2 [25]. They showed the strong increase of $\sigma_{v\to DA}$ for $E(v) < V(R_c)$, but rather found a stagnation than a decrease of $\sigma_{v\to DA}$ for $E(v) > V(R_c)$.

For the calculation of the temperature-dependent cross section according to Eq. (21) it was sufficient to include $\sigma_{v\to DA}$ up to $v = 9$; the use of higher vibrational levels did not change the results. Figs. 4a and 4b show the experimental and calculated data, respectively. The calculated data possess peaks for the vibrational levels v in the energy ranges where the corresponding $\sigma_{v\to DA}$ have their maxima. This is an artifact of the quantization introduced in Eq. (17), yet it helps to understand the features of the calculated cross sections. $\sigma_{0\to DA}$ determines $\sigma_{DA}(T = 300\ K)$ and its maximum becomes the center of the peak at ≈ 1.4 eV. The increased population of $v = 1$ at $T = 800$ K causes the shift of this peak to lower energies and its increase in intensity. The additional substantial population of $v = 5$ at $T = 800$ K gives rise to the threshold peak near 0 eV. After all, the strong influence of the population of the vibrational states on $\sigma_{DA}(T)$ is only possible because of the great increase of the $\sigma_{v\to DA}$ versus v, which again is a result of the location of the crossing point, such that the latter originally causes the temperature effects in $\sigma_{DA}(T)$. Similar observations were made by Fabrikant in an R-matrix analysis of DA for the example molecule CH_3Cl [26–28].

The experimental data presented in Fig. 4a were taken from Hahndorf et al. [13]. Their absolute values were adapted according to Ref. [14], the data of which were corrected for the temperature effect using Ref. [12]. The sizes of the calculated peaks differ from the experimental ones by approximately a fac-

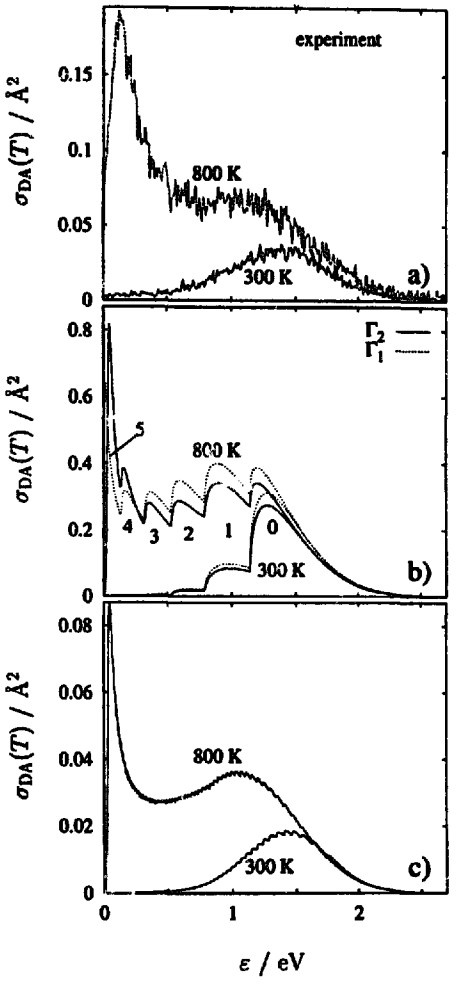

Fig. 4. The dissociative cross sections $\sigma_{DA}(T)$ for $T = 300$ K and $T = 800$ K. (a) Experimental. The data were taken from Ref. [13] and their absolute values adapted such that the peak size in σ_{DA} (300 K) corresponds to the value given in Ref. [14], corrected for the temperature effect according to Ref. [12]. (b) Calculated with Γ_1 and Γ_2. The numbers denote the vibrational levels v that give the main contribution. (c) $\sigma_{DA}(T)$ calculated with Γ_2 and with a quantization $n = 10$ times smaller than the 'true' vibrational level range.

tor of 8. But there may be some uncertainty of the underlying measurement in Ref. [14], as was explained above. On the other hand, it is possible that the anion potential used here might be too steep. A less steep potential would reduce the velocity in the anion state and thus cause a smaller survival probability. This would finally result in a smaller cross section.

The good relative agreement between theory and experiment becomes even more visible, if a smaller quantisation is introduced, such that the interval $[E_{vib}(v-\frac{1}{2}), E_{vib}(v+\frac{1}{2})]$ is divided into n parts. Because of Eq. (17) this gives rise to a decrease of absolute values of $\sigma_{v\to DA}$ and $\sigma_{DA}(T)$ by a factor of n, but the relative cross sections converge as indicated in Fig. 4c.

5. Conclusion

It was shown that it is possible to explain temperature effects in the dissociative cross section of CF_3Cl within a simple classical theory in a one-dimensional model. It was stressed that for the existence of these effects it is necessary that the crossing point of the potential curves of the neutral molecule and the anion lies in an energy range accessible by heating the system. The calculations lead to the conclusion that for impact energies close to 0 eV molecules prepared (e.g. by laser excitation) in the vibrational states $v = 5, 6$ should give a high yield of the dissociation products.

The theory is extendable also to (resonant) elastic and inelastic scattering. The calculation of the peak sizes and positions in the respective cross sections will be useful to check the consistency of the theory with the experiments. A calculation of the ratio of single vibrational excitation to overtones will also be of importance, since it is known that the inelastic cross section is mainly due to single VE ($v = 0 \to v = 1$) [7]. It is also desirable to describe the overall process in a more thorough quantum-mechanical approach. Work along this line is also in progress.

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